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Task 1 Report
Target Vapor Identification and Database Development

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July 1993

Technical Report

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13. ABSTRACT *(Maximum 200 words)*

This report covers "Task 1: Target Vapor Identification and Database Development" for the program "Development of a Handheld Chemical Detector Using Microchip GC." The study described in this report addresses the performance requirements for the concept handheld instrument for vapor detection of CW-related material using microchip GC. Included in this study is a survey of the volatiles and semivolatiles included in Schedules 1, 2 and 3 from the draft convention for CW treaty verification. The concept approach and estimated operational requirements are discussed with respect to these materials. Experimental measurements are presented using representative schedule materials and simulants for volatile and semivolatile CW agents in Schedule 1. These measurements demonstrate the desired chemical selectivity required for the concept instrument and "bracket" the chromatographic performance requirements. Instrument operation in two regimes is likely to be required in the concept instrument based upon these results. A likely instrument configuration would contain two small, fast GC modules operated at different temperatures, and each module performing highly selective chemical identification through correlated gas chromatography.

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CONVERSION TABLE

Conversion factors for U.S. customary to metric (SI) units of measurement.

To Convert From	To	Multiply By
angstrom	meters (m)	1.000 000 X E -10
atmosphere (normal)	kilo pascal (kPa)	1.013 25 X E +2
bar	Xilo pascal (kPa)	1.000 000 X E +2
barn	meter^2 (m^2)	1.000 000 X E -28
British thermal unit (thermochemical)	joule (J)	1.054 350 X E +3
cal (thermochemical)/cm^2$	mega joule/m^2 (MJ/m^2)	4.184 000 X E -2
calorie (thermochemical)$	joule (J)	4.184 000
calorie (thermochemical)/g$	joule per kilogram (J/kg)*	4.184 000 X E +3
curie$	giga becquerel (GBq)†	3.700 000 X E +1
degree Celsius‡	degree kelvin (K)	$t_K = t°_C + 273.15$
degree (angle)	radian (rad)	1.745 329 X E -2
degree Fahrenheit	degree kelvin (K)	$t_K = t°_F + 459.67)/1.8$
electron volt$	joule (J)	1.602 19 X E -19
erg$	joule (J)	1.000 000 X E -7
erg/second	watt (W)	1.000 000 X E -7
foot	meter (m)	3.048 000 X E -1
foot-pound-force	joule (J)	1.355 818
gallon (U.S. liquid)	meter^3 (m^3)	3.785 412 X E -3
inch	meter (m)	2.540 000 X E -2
jerk	joule (J)	1.000 000 X E +9
joule/kilogram (J/kg) (radiation dose absorbed)$	gray (Gy)*	1.000 000 X E +91
kilotons$	terajoules	4.183
kip (1000 lbf)	newton (N)	4.448 222 X E +3
kip/inch^2 (ksi)	kilo pascal (kPa)	6.894 757 X E +3
ktap	newton-second/m^2 (N-s/m^2)	1.000 000 X E +2
micron	meter (m)	1.000 000 X E -6
mil	meter (m)	2.540 000 X E -5
mile (international)	meter (m)	1.609 344 X E +3
ounce	kilogram (kg)	2.834 952 X E -2
pound-force (lbf avoirdupois)	newton (N)	4.448 222
pound-force inch	newton-meter (N•m)	1.129 848 X E -1
pound-force/inch	newton/meter (N/m)	1.751 268 X E +2
pound-force/foot^2	kilo pascal (kPa)	4.788 026 X E -2
pound-force/inch^2 (psi)	kilo pascal (kPa)	6.894 757
pound-mass (lbm avoirdupois)	kilogram (kg)	4.535 924 X E -1
pound-mass-foot^2 (moment of inertia)	kilogram-meter^2 (kg•m^2)	4.214 011 X E -2
pound-mass/foot^3	kilogram-meter^3 (kg/m^3)	1.601 846 X E +1
rad (radiation dose absorbed)$	gray (Gy)*	1.000 000 X E -2
roentgen$	coulomb/kilogram (C/kg)	2.579 760 X E -4
shake	second (s)	1.000 000 X E -8
slug	kilogram (kg)	1.459 390 X E +1
torr (mm Hg, 0°C)	kilo pascal (kPa)	1.333 22 X E -1

*The gray (Gy) is the accepted SI unit equivalent to the energy imparted by ionizing radiation to mass of energy corresponding to joule/kilogram.
†The becquerel (Bq) is the SI unit of radioactivity; 1 Bq = 1 event/s.
‡Temperature may be reported in degree Celsius as well as degree kelvin.
$These units should not be converted in DNA technical reports; however, a parenthetical conversion is permitted at the author's discretion.

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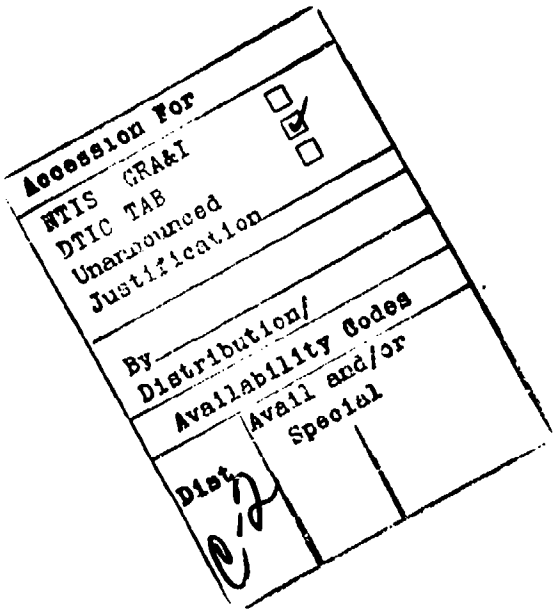

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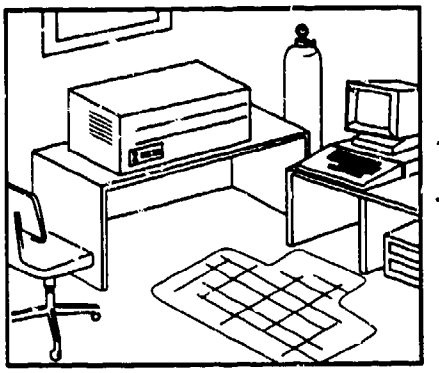
SECTION 1
INTRODUCTION

The proliferation of chemical weapons technology poses a significant threat to peace and stability in the post Cold-War world. This has been recognized by the numerous parties that negotiated the Chemical Weapons Convention, which should be offered for signature in January 1993. A key part of this treaty is the provision for on-site challenge inspections for the presence of prohibited Chemical Weapons (CW) and pre-cursor chemicals.

The treaty specifics that, "where possible, the analysis of samples shall be performed on-site." Since the allowable time for challenge inspections under the treaty is limited, this places a premium on rapid, accurate analysis for treaty prohibited materials. It is also expected that challenge inspections will be requested by foreign governments at U.S. sites where proprietary industrial and sensitive military research and/or production are being carried out, and thus the analysis of samples with general purpose techniques such as Gas Chromatography/Mass Spectrometry (GC/MS) might be deliberately used to probe for important information about commercial and military projects unrelated to chemical weapons. This situation poses significant legal and security questions concerning U.S. industrial competitiveness and national security, and places a high premium on the development of inspection technologies which will provide accurate analyses for treaty prohibited materials *without* revealing the identity of other chemical compounds.

The present program to develop a handheld chemical detector for treaty inspections using microchip GC (μGC) technology is designed to address these needs and concerns. General Research Corporation's (GRC's) program concept (Figure 1-1) is to translate much of the functional capability of benchtop GC/MS laboratory instrumentation into a handheld miniaturized correlated column GC instrument that can be trained with software for fast, accurate recognition of the presence of treaty prohibited materials.

GC/MS instrumentation is comparatively large, delicate, power hungry, and its operation requires significant technical training and user expertise. Individual runs typically



GC/MS Laboratory Instrument

- Large
- Not Easily Portable
- Complex Method & Operation
- User Technical Background Required

Capture Analytical Functions In Miniaturizable Components

Translate Capability Train With Software

Hand Held CW Detector

- Related GC Technology as its Foundation
- Fast, On-Site Analysis
- Simplified Method & Operation
- No Technical Background Required for Users

Figure 1-1. Program concept.

take 30 minutes or more, without data interpretation. These features tend to make GC/MS technology "van" or "cart" portable at best, and relatively slow, allowing only a limited number of samples to be run during a challenge inspection. Since GC/MS results generally include mass spectra of all the compounds detected, inspection results might be readily diverted from authorized treaty verification purposes to the gathering of intelligence information on proprietary commercial processes or sensitive non-CW related military R&D. This poses a potential problem for all parties to the treaty, but may be especially threatening to the U.S. and other Western industrialized nations.

μGC instrumentation on the other hand is very compact, robust, and consumes little power, making it well suited for handheld instrument development. Chemical separations made with μGC are typically completed in seconds rather than the minutes required for ordinary GC separations (see Figure 1-2). A key requirement for treaty verification applications is a high degree of selectivity for accurate identification of prohibited CW weapon and pre-cursor chemicals. This can be achieved by "correlated column" GC using

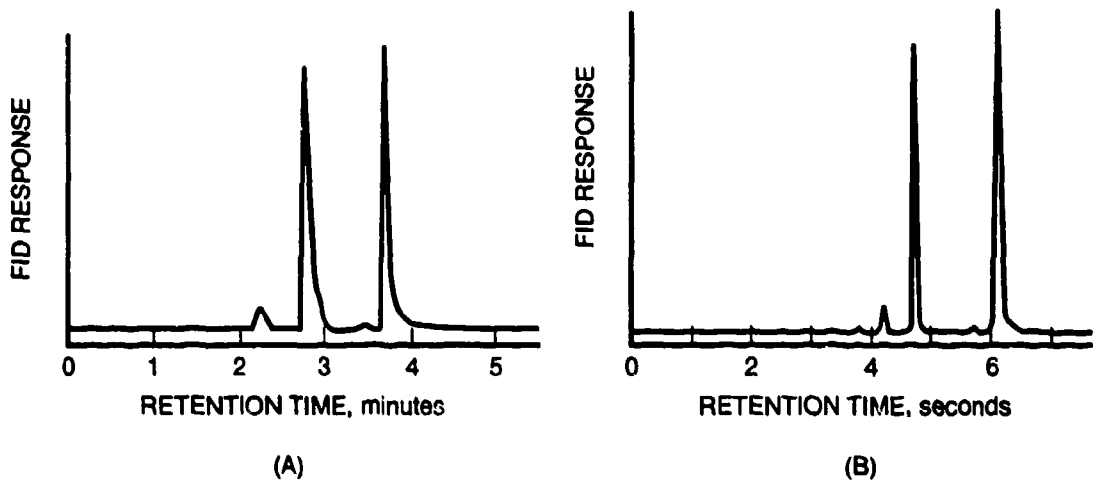


Figure 1-2. Comparison of a conventional chromatogram (A) and a fast chromatogram (B) for a mixture of benzene, toluene, and xylene run under similar conditions.

multiple μGCs with different column types integrated into the same instrument and run simultaneously. Properly implemented, this approach expands "detection space" from the single dimension of ordinary GC to 2 or more "dimensions" in the correlated chromatogram and thus greatly reduces overlap ambiguity between different compounds (see Figure 1-3).

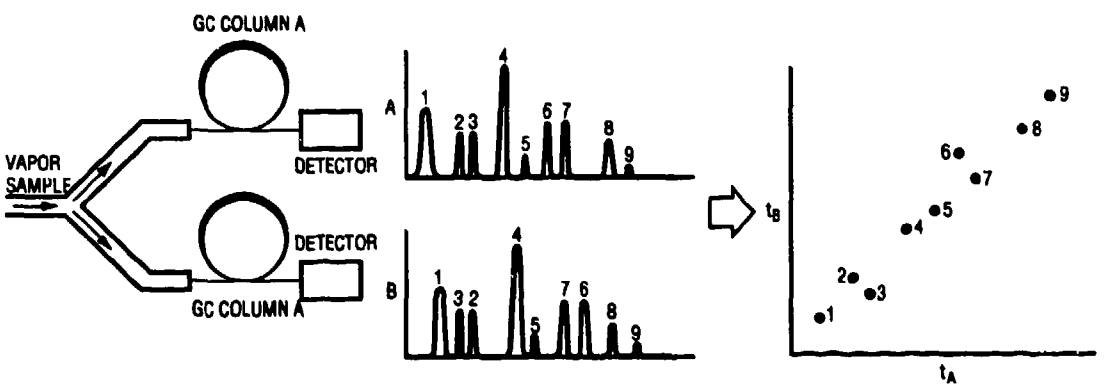


Figure 1-3. Correlation of two different chromatograms for a sample and the corresponding 2-dimensional detection space.

The search for a particular compound in an unknown sample is made by checking the known retention time "coordinates" for that compound in "detection space" to see if it is present. An unknown compound *cannot* be identified unless it has previously been prepared and run under the same temperature and conditions on the same combination of column types to determine its own "unique coordinates" in detection space. This feature greatly reduces the possibility of using data from treaty inspections to identify proprietary compounds or processes. The ability to go to multiple correlated columns in a handheld instrument is made feasible because μGC technology is so light and compact.

GRC's instrument concept is to develop a rugged handheld instrument for treaty inspections based on μGC components and related technology. Based on our current understanding of operational needs for challenge inspections we have set the following estimated requirements:

- **Sensitivity.** Current μGC instruments using miniature thermal conductivity detectors have a sensitivity of about 1 ppm or below. With preconcentration by adsorbent traps, sensitivity gains in the range of 100-300x can be realized. This can give μGC the desired sensitivity in the low ppb range. An important technical objective then becomes the development and demonstration of an adsorbent trap which can cycle at the analysis speed set by the requirements. Microtraps have been demonstrated for μGC and our objective will be to tailor a microtrap to meet the requirements.

- **Selectivity.** Current fast GC instruments including μGC have demonstrated the ability to provide chemical separations comparable to conventional GC. The ability to generate a highly selective unique 2-D or higher dimensional correlated GC database for the identification of CW-related materials by a μGC is not expected to present a problem since these materials have been successfully studied and routinely measured in the past by chromatographic methods. Our expectation is that correlated chromatography will provide the chemical selectivity necessary for the handheld CW detector.

- **Analysis cycle speed.** GRC's technical objective is to develop a preconcentrator which can cycle to match the analysis time of the μGC instrument. The analysis time of the μGC is on the order of 10's of seconds for many volatiles, but this is a sensitive function of molecular properties and temperature, other things being equal. Fast, low power operation of a μGC may require relatively cooler isothermal GC operation which can lengthen analysis times. While this is a trade-off to be made in the design of the concept instrument, it is expected that analysis cycle times on the order of one minute should be feasible. The functional element evaluation of microtraps leading to the specific microtrap design will determine the heating, cooling, and sampling times possible for the microtraps. With small sample volumes and low thermal masses, it is anticipated that microtrap cycling in the same time frame should be possible.

- **Size/Weight.** GRC's objective is to make the handheld detector as small as possible. Given the size of the components, it is our estimate that it should be possible to fit the correlated μGC module, detector, electronics for signal processing and instrument control, and preconcentrator in a "lunchbox" size instrument, i.e. 12 in x 6 in x 6 in. Further size reduction may be possible, but the power requirement for this concept instrument is yet to be established. This will be established in the course of the concept instrument definition and will determine the added weight (and possibly size) required for batteries. We have estimated approximately 10 lbs for the weight requirement, since above this weight an instrument becomes too heavy for handheld use. Our research and design efforts will be to reduce weight where possible within the scope of fabricating and demonstrating a prototype, but our program emphasis will be the successful demonstration of a prototype which meets first the sensitivity, selectivity, speed, and size requirements. The final design analysis of the prototype will include an analysis of possible further weight reductions through the substitution of light weight materials for housing components, for example, which would be an important consideration in preproduction engineering development.

- **Ease of Use.** Our objective will be to design the instrument for ease of use by personnel possessing minimal technical training. We believe this can be achieved by the use of onboard advanced signal processing algorithms, to recognize the presence or absence of signatures related to treaty prohibited materials, along with establishing simplified sampling protocols for inspection use.

- **Ruggedization.** GRC's objective will be to demonstrate the suitability of the prototype technology for ruggedization. This will include both resistance to shock (rough handling) and operation under a wide range of environmental conditions (i.e. temperature, humidity, and industrial chemical environments). It should be noted that an earlier μGC instrument has been developed for NASA to meet launch load requirements.

SECTION 2
LITERATURE REVIEW/ANALYSIS

The initial subtask of Task 1 was the review of available literature to determine the chromatographic information available on the target CW materials. Since much research has already been conducted with the common CW materials of concern, information from this research can provide indications of: the chromatographic properties of different CW materials on different GC media; suitable chromatographic simulants for the CW materials; chemical and physical properties; and the behavior of these CW materials when used with adsorbent trapping materials. Information sources include both the open literature and government reports. The large amount of open literature was accessed through on-line databases such as Dialog and Current Contents. Dialog itself consists of a large number of databases. Technical references concerning specific CW materials were obtained primarily from the Chemical Abstracts database within Dialog using searches by Chemical Abstracts Services registry numbers.

The focus of the CW detection effort are the CW materials and synthetic precursors specified by the *Conference on Disarmament: Draft Convention on the Prohibition of the Development, Production, Stockpiling and Use of Chemical Weapons and on Their Destruction* in Schedules 1, 2 and 3. The Schedule 1 list consists of toxic chemicals which have no significant use outside of CW. This list, shown in Table 2-1 with CAS registry numbers, includes many historical CW agents as well as CW precursors whose only utility is the synthesis of Schedule 1 materials. The Schedule 2 materials are toxic chemicals or important CW synthetic precursors which are used in very limited quantities for commercial purposes which are not prohibited by the convention. These materials are listed in Table 2-2. Schedule 3 materials are those that present risk as either CW materials or CW precursors, but are produced in large quantities for commercial uses not prohibited under the convention. The Schedule 3 materials are listed in Table 2-3.

In order for a handheld detector using fast GC methods to detect these materials, the GC must be operated at sufficient temperatures to rapidly elute the less volatile materials.

Table 2-1. Schedule 1 CW compounds.

		(CAS registry Number)
A.	**Toxic chemicals:**	
(1)	O-Alkyl ($\leq C_{10}$, incl. cycloalkyl) alkyl (Me, Et, n-Pr or i-Pr)-phosphonofluoridates	
	e.g. Sarin: O-Isopropyl methylphosphonofluoridate	(107-44-8)
	Soman: O-Pinacolyl methylphosphonofluoridate	(96-64-0)
(2)	O-Alkyl ($\leq C_{10}$, incl. cycloalkyl) N,N-dialkyl (Me, Et, n-Pr or i-Pr) phosphoramidocyanidates	
	e.g. Tabun: O-Ethyl N,N-dimethyl phosphoramidocyanidate	(77-81-6)
(3)	O-Alkyl (H or $\leq C_{10}$, incl. cycloalkyl) S-2 dialkyl (Me, Et, n-Pr or i-Pr)-aminoethyl alkyl (Me, Et, n-Pr or i-Pr) phosphonothiolates and corresponding alkylated or protonated salts	
	e.g. VX: O-Ethyl S-3-diisopropylaminoethyl methyl phosphonothiolate	(50782-69-9)
(4)	Sulfur mustards:	
	2-Chloroethylchloromethylsulfide	(2625-76-5)
	Mustard gas: Bis(2-chloroethyl)sulfide	(505-60-2)
	Bis(2-chloroethylthio)methane	(63869-13-6)
	Sesquimustard: 1,2-Bis(2-chloroethylthio)ethane	(3563-36-8)
	1,3-Bis(2-chloroethylthio)-n-propane	(63905-10-2)
	1,4-Bis(2-chloroethylthio)-n-butane	(142868-93-7)
	1,5-Bis(2-chloroethylthio)-n-pentane	(142868-94-8)
	Bis(2-chloroethylthiomethyl)ether	(63918-90-1)
	O-Mustard: Bis(2-chloroethylthioethyl)ether	(63918-89-8)
(5)	Lewisites:	
	Lewisite 1: 2-Chlorovinyldichloroarsine	(541-25-3)
	Lewisite 2: Bis(2-chlorovinyl) chloroarsine	(40334-69-8)
	Lewisite 3: Tris(2-chlorovinyl)arsine	(40334-70-1)
(6)	Nitrogen mustards:	
	HN1: Bis(2-chloroethyl)ethylamine	(538-07-8)
	HN2: Bis(2-chloroethyl)methylamine	(51-75-2)
	HN3: Tris(2-chloroethyl)amine	(555-77-1)
(7)	Saxitoxin	(35523-89-8)
(8)	Ricin	(9009-86-3)
B.	**Precursors:**	
(9)	Alkyl (Me, Et, n-Pr or i-Pr) phosphonyldifluorides	
	e.g. DF: Methylphosphonyldifluoride	(676-99-3)
(10)	O-Alkyl (H or $\leq C_{10}$, incl. cycloalkyl) 0-2 dialkyl (Me, Et, n-Pr or i-Pr)-aminoethyl alkyl (Me, Et, N-Pr or i-Pr) phosphonites and corresponding alkylated or protonated salts	
	e.g. QL: O-Ethyl 0-2-diisopropylaminoethyl methylphosphonite	(57856-11-8)
(11)	Chlorosarin: O-Isopropyl methylphosphonochloridate	(1445-76-7)
(12)	Chlorosaman: O-Pinacolyl methylphosphonochloridate	(7040-57-5)

Table 2-2. Schedule 2 CW compounds.

		(CAS registry number)
A.	**Toxic chemicals:**	
(1)	Amiton: 0,0-Diethyl S-[2-diethylamino)ethyl] phosphorothiolate and corresponding alkylated or protonated sales	(78-53-5)
(2)	PFIB: 1,1,3,3,3-Pentafluoro-2-(trifluoromethyl)-1-propene	(382-21-8)
(3)	BZ: 3-Quinuclidinyl benzilate	(6581-06-2)
B.	**Precursors:**	
(4)	Chemicals, except for those listed in Table 2-1, containing a phosphorus atom to which is bonded one methyl, ethyl or propyl (normal or iso) group but not further carbon atoms, e.g. Methylphosphonyl dichloride Dimethyl methylphosphonate Exemption: Fonofos: 0-Ethyl S-phenyl ethylphosphono-thiolothionate	 (676-97-1) (756-79-6) (944-22-9)
(5)	N,N-Dialkyl (Me, Et, n-Pr or i-Pr) phosphoramidic dihalides	
(6)	Dialkyl (Me, Et, n-Pr or i-Pr) N,N-dialkyl (Me, Et, n-Pr or i-Pr)-phosphoramidates	
(7)	Arsenic trichloride	(7784-34-1)
(8)	2,2-Diphenyl-2-hydroxyacetic acid	(76-93-7)
(9)	Quinuclidine-3-ol	(1619-34-7)
(10)	N,N-Dialkyl (Me, Et, n-Pr or i-Pr) aminoethyl-2-chlorides and corresponding protonated salts	
(11)	N,N-Dialkyl (Me, Et, n-Pr or i-Pr) aminoethane-2-ols and corresponding protonated salts Exemptions: N,N-Dimethylaminoethanol and corresponding protonated salts N,N-Diethylaminoethanol and corresponding protonated salts	 (108-01-0) (100-37-8)
(12)	N,N-Dialkyl (Me, Et, n-Pr or i-Pr) aminoethane-2-thiols and corresponding protonated salts	
(13)	Thiodiglycol: Bis(2-hydroxyethyl)sulfide	(111-48-8)
(14)	Pinacolyl alcohol: 3,3-Dimethylbutane-2-ol	(464-07-3)

Table 2-3. Schedule 3 CW compounds.

		(CAS registry number)
A.	**Toxic chemicals:**	
(1)	Phosgene: Carbonyl dichloride	(75-44-5)
(2)	Cyanogen chloride	(506-77-4)
(3)	Hydrogen cyanide	(74-90-8)
(4)	Chloropicrin: Trichloronitromethane	(76-06-2)
B.	**Precursors:**	
(5)	Phosphorus oxychloride	(10025-87-3)
(6)	Phosphorus trichloride	(7719-12-2)
(7)	Phosphorus pentachloride	(10026-13-8)
(8)	Trimethyl phosphite	(121-45-9)
(9)	Triethyl phosphite	(122-52-1)
(10)	Dimethyl phosphite	(868-85-9)
(11)	Diethyl phosphite	(762-04-9)
(12)	Sulfur monochloride	(10025-67-9)
(13)	Sulfur dichloride	(10545-99-0)
(14)	Thionyl chloride	(7719-09-7)
(15)	Ethyldiethanolamine	(139-87-7)
(16)	Methyldiethanolamine	(105-59-9)
(17)	Triethanolamine	(102-71-6)

At the same time, the instrument must still be able to resolve the most volatile materials of interest. For the purposes of defining the instrument's GC technical performance requirements, the literature review was focused on determining the chromatographic properties of materials in the schedules which best bound the performance requirements of the concept correlated GC instrument. The primary performance boundary to define is the range of temperatures required for fast GC operation for the less volatile materials in the schedules. Secondarily, the separations achievable for the different materials must be considered at various temperatures to ensure that both the volatiles and the semivolatiles can be sufficiently

separated. This analysis also includes the choice of GC stationary phases to provide good separations and discrimination against background. Another consideration is the reversibility with which these compounds adsorb onto trapping materials during preconcentration before GC separation and detection.

Current practice in defining the boundary between volatiles and semivolatiles is to define the semivolatiles as compounds having vapor pressures below 1 mm of mercury (i.e. 1 torr) at standard temperature and pressure (0°C, 1 atmosphere pressure). For the series of straight-chain hydrocarbons (n-alkanes), the volatile range extends to decane ($C_{10}H_{22}$) at ordinary laboratory temperatures (20-25°C). Inspection of the compounds in Schedules 1, 2 and 3 (shown in Tables 2-1, 2-2 and 2-3) shows about an even mix of volatiles and semivolatiles, with a few compounds which are better classified as nonvolatiles. These nonvolatile materials are solids at room temperature and the vapor pressures are expected to be far too low for practical vapor detection. These nonvolatiles include saxitoxin and ricin (high molecular weight proteins), 3-quinuclidinyl benzilate (BZ; melting point of 164-165°C), and quinuclidine-3-ol (a BZ precursor; melting point 223-224°C). Problems may also exist for the salt forms of a few materials in the schedules. While the base materials are likely to be detectable as volatiles or semivolatiles by the concept instrument, in the form of protonated salts their vapor pressures may be greatly reduced. However, as salts these materials may still be detectable due to residual volatiles in the salts, decomposition, or the possible generation of volatiles by hydrolysis.

The elution profile of a number of volatile and semivolatile CW compounds relative to decane is illustrated in Figure 2-1 (Witkiewicz, 1990). This separation of CW ag nts was performed on a DB-5 capillary column using a programmed temperature ramp from 30°C to 220°C. Both sarin (GB) and soman (GD) elute near or before $C_{10}H_{22}$, while VX, one of the less volatile of the CW agents, elutes very close to $C_{17}H_{36}$. While the volatility of GB is 22,000 mg/m^3 at 25°C, the volatility of VX is only 10.5 mg/m^3 (NRC, 1984). The vapor pressures corresponding to these volatilities are approximately 0.4 kPa (3 torr) and 1.3×10^{-4} kPa (10^{-3} torr), respectively. Thus, VX is a good example of one of the less volatile CW agents which the concept instrument must be capable of detecting. As suggested by Figure

2-1, $C_{17}H_{36}$ would provide a retention time simulant for VX. Further, the use of the C_{17}-C_{20} hydrocarbons would provide a good test of the GC performance of a concept for separation of the least volatile CW agents of interest at acceptable speeds of operation.

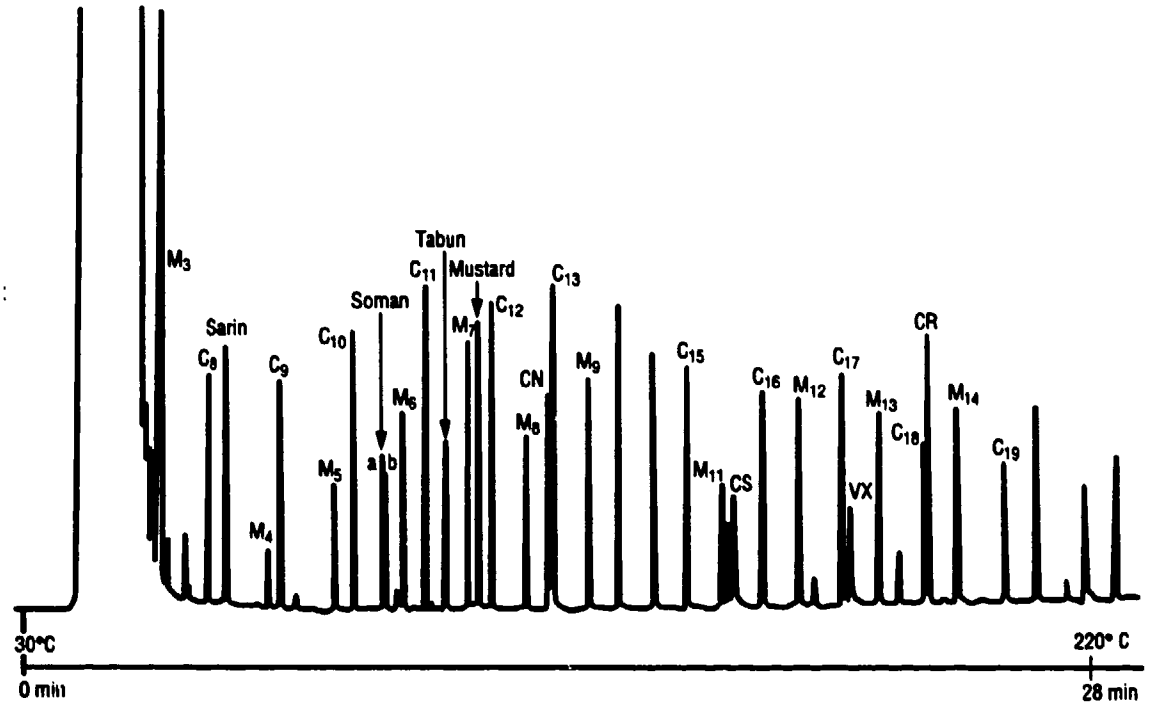


Figure 2-1. Elution of CW agents relative to standards (Witkiewitz, 1990).

The chromatographic properties of a number of the materials listed in the CW material schedules are characterized in the literature with regards to specific GC phases by retention indices, the standard being based upon the Kovat's Retention Index system. The Kovat's retention indices are determined by the retention time of a compound with respect to the retention times for a series of normal alkanes (e.g., hexane, heptane, octane, etc.). For the n-alkanes the logarithm of the adjusted retention time (the measured retention time corrected for the column dead time) is a linear function of the number of carbon atoms in the molecule. By definition, the retention index of the n-alkanes is 100 times the number of carbon atoms in the molecule (e.g., 600 for hexane, 700 for heptane, 800 for octane, etc.). Thus, where retention indices have been measured for CW compounds, these can be used to determine n-alkanes which are retention time simulants. In this way, the separation speed requirements

for the semivolatile CW materials by a concept instrument can be investigated using the appropriate alkane simulants.

Some retention indices for CW materials in the schedules which were obtained from searching the technical literature are listed in Table 2-4. While data are available for a variety of different chromatographic stationary phases, only those applicable to DB-5, a standard nonpolar phase, are listed in Table 2-4. VX and T represent two of the least volatile agents, and a detector which was capable of rapid chromatographic analysis with alkanes ranging as high as C_{17} to C_{19} would be capable of detecting the most difficult semivolatiles in the schedules.

Table 2-4. DB-5 retention indices for selected CW materials.

Compound	Retention Index	References
Sarin (GB)	824 817	a,b c
Soman (GC)	1045,1049 (enantiomeric pair) 1038,1042	a,b c
Me,2-Methylcyclohexyl phosphonofluoridate	1257,1258 (enantiomeric pair)	a
Tabun (GA)	1132	a
VX	1710	a
HD	1124	a,b
Q	1689	a,b
T	1980 1983	a b
1,4-Thioxane (HD-related product)	880	a,b
1,4-Dithiane (HD-related product)	1060	a,b
Thiodiglycol	1182	a,b
2-(Diisopropylamino) ethanethiol	1114	a

(References: a = D'Agostino, 1985; b = D'Agostino, 1988; c = Hancock, 1991)

When a chromatograph is operated at sufficient temperature to provide rapid chromatographic separations of the most difficult semivolatile CW compounds described above, the separation (or even the detection) of the light volatiles may become difficult because these materials may elute too rapidly for good resolution. Many of the CW compounds in the schedules are such volatiles. The boiling points of several of these compounds are listed in Table 2-5. With such low boiling points these materials are very volatile and will rapidly vaporize from the liquid state at standard room temperatures. They are expected to elute rapidly, although their chemical reactivity suggests that their likely decomposition during thermal desorption will create new signature compounds for detection by gas chromatography. Both hydrogen cyanide and phosgene have been reported to be strongly adsorbed by adsorbent traps and undergo decomposition during the thermal desorption process resulting in "ghost" peaks (Witkiewicz, 1990). These peaks may still function as signatures for the detection of these compounds. Silanizing the injection system has also been suggested to reduce the decomposition of these chemically reactive compounds.

Table 2-5. Boiling points of selected low molecular weight CW compounds.

Compound	Molecular Weight	Boiling Point, °C (1 atm pressure)
Hydrogen cyanide	27.0	25.7
Cyanogen chloride	61.5	12.6
Phosgene	98.9	8.2
Thionyl chloride	119	79

Based upon the large number of volatiles in the schedules including the very light volatiles in Table 2-5, it is likely that the concept instrument may require two miniature GC modules: a module capable of operating at a sufficiently high temperature that the heaviest semivolatiles of interest will elute quickly, and a low temperature module which will separate the volatiles for detection. It is expected that the current state-of-the-art technology can be directly adapted to provide the miniature GC module for the low temperature, fast separation of the volatiles since this type of separation has been demonstrated with other classes of

materials spanning a similar range of volatilities. The use of multiple modules was proposed for the detector in order to achieve correlation chromatography as well as to cover simultaneous operation in different temperature regimes.

Background organic vapors which could cause possible interferences are expected to originate from the industrial settings in which challenge inspections could be conducted. For example, the diversion of chemical operations in a organophosphorus insecticide manufacturing facility would be one of the probable means for a country to produce nerve agents. In such a setting, a large number of possible background vapors are clearly possible depending upon the particular manufacturing setting. Interestingly, correlated chromatography can provide excellent separation and discrimination against such backgrounds, especially by using three or more simultaneous dimensions for operation. Focusing just on volatiles of interest to the EPA, Dr. Overton's group at Louisiana State University (LSU) has demonstrated that 94% of their entire database can be discriminated by 2-dimensional correlated chromatography. This was achieved using stationary phases which did not differ in their separation capabilities as much as the phases we are proposing. Further, their work suggests that adding a third correlated GC column of a yet different nature would fully separate the entire database. This should be contrasted with the performance of GC/MS: while GC/MS uses retention times in one dimension and the mass spectrum in a second dimension to provide essentially a 2-dimensional separation technique, the mass spectral dimension often fails to discriminate between chemically related compounds when the signals are not strong because the differences in the reference spectra are slight relative to the noise. In fact, many chemically-related series of compounds are difficult to tell apart using GC/MS due to the close similarities of their spectra when using standard ionization techniques such as electron impact. Combined with the frequent overlap of compounds in a chromatogram (incomplete separations), this can greatly complicate the interpretation of the GC/MS results. Based upon the research at LSU, 3-dimensional separations using correlated chromatography appear to provide sufficient separation and discrimination capability to result in very low false positives in a high background environment.

Besides chemical background due to production chemicals such as organophosphate insecticides, the common volatiles monitored by the EPA are likely to constitute some of the most common background air volatiles. Such volatiles can be sampled from city air, chemical storage sites, and chemical laboratories. Correlated chromatography databases exist for these common volatiles (Overton, 1991), and these data should be augmented so they can be applied to the GC stationary phases which are applied to the detection of the CW compounds. This can be accomplished through air sampling and correlation analysis with developmental μGC instrumentation.

SECTION 3
EXPERIMENTAL TECHNIQUE DEVELOPMENT

3.1 CORRELATED GC

Ordinary one-dimensional GC is a standard laboratory separation method, but it is generally not a sufficiently selective detection method for the wide range of compounds that may be encountered in treaty verification applications without being coupled to a selective detector such as a mass spectrometer in GC/MS. The selectivity of our concept μGC instrument for CW detection results from the use of correlated chromatography. In correlated chromatography, a sample consisting of a mixture of compounds is subjected to analysis by two or more GC columns which differ in the chemical separations they perform. These differences in separation performance are usually achieved through different chemical compositions of the coatings ("stationary phases") on the inner wall of the GC column.

A common combination of stationary phases for correlated chromatography, for example, might be a column having a nonpolar (hydrocarbon-like) stationary phase and a column having a more polar stationary phase. When the same mixture is separated on each column, the two chromatograms differ in both the times in which given components come off the column (the "elution" time) and often can differ in the sequence in which the components elute from the column. When the elution times of the components for both columns are plotted against each other, the differences between the columns results in "scattering" in the plots. This was conceptually illustrated in Figure 1-3 for two hypothetical chromatograms for a nine component mixture. Since the stationary phase for column B differs from column A, some shifts in the elution times are represented including some reordering of the elution sequence of these compounds. When the elution times are plotted for the two different columns, the resulting points exhibit off-diagonal "scattering" in the plot. If the two columns were identical in their separations, the resulting plot would be perfectly linear with all points falling on the same line.

It is the scattering in 2 dimensions illustrated in Figure 1-3 which is responsible for the selectivity of correlated GC. Two compounds which might coincidentally elute at the same time on one stationary phase are unlikely to co-elute on a different stationary phase, especially when the second stationary phase is chosen to differ substantially in its separation characteristics relative to the first column. The greater the degree of dispersion of the chromatographic correlations in the 2-dimensional plot is, the greater the selectivity of the correlated chromatography is expected to be. In the example in Figure 1-3, the stationary phases actually differ only slightly in their separation performance relative to the actual separations resulting from stationary phase pairings chosen to maximize the differences. In optimized systems, the dispersion is relatively large. Further, different GC detectors can be used with each column to provide additional chemical selectivity in correlated GC.

Examples of the selectivity and utility of correlated GC are provided by published reports of correlated GC applications. The Central Forensic Laboratory of the Royal Canadian Mounted Police (RCMP) in Canada studied the performance of correlated dual-column capillary GC instruments applied to the detection of illicit drugs (Perrigo, 1985). They studied the performance of their instrument using 188 target compounds for forensic drug screening. Different detectors were used to enhance the selectivity of the instrument (flame ionization and nitrogen-phosphorus detectors). Both elution times and relative detector responses were determined for all of the compounds of interest. Using elution times only, their selectivity was between 96.6-99.4% depending upon the allowed margin of error; i.e., only 0.6-3.4% of the 188 compounds were not resolvable in the database. Combining the response of the detectors reduced the ambiguity of the database to less than 1% of the 188 compounds. This work demonstrates that very favorable selectivity can be obtained with dual column chromatography.

Another published example showing an application of dual-column correlated chromatography to the detection of drugs is provided by the Swedish Laboratory of Forensic Science (Alm, 1983). These studies preceded the RCMP studies discussed above using a similar experimental approach with the same types of detectors. Figure 3-1 shows a pair of correlated chromatograms from their study. They reported that the spread of the values was

large compared to the size of the detection windows, and the risk of accidental overlap was small. They tested their system by recording mass spectra in parallel with the GC runs during a six month period involving more than 2000 casework samples. For the approximately 80 compounds in the database, there were no cases of false positives registered by the correlated GC for these 2000 samples.

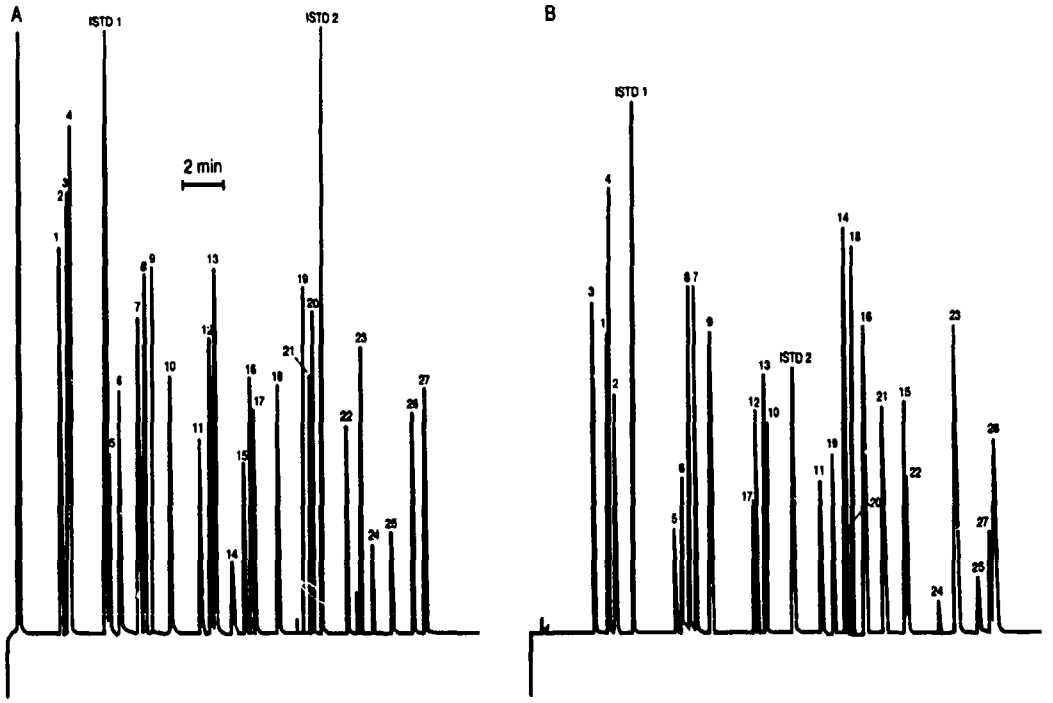
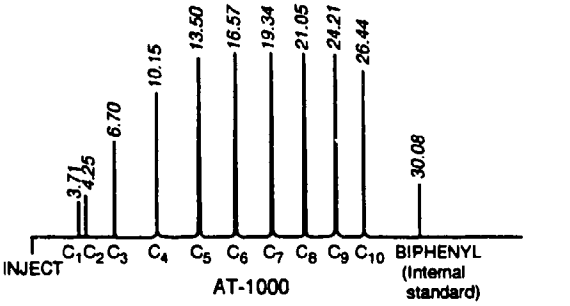
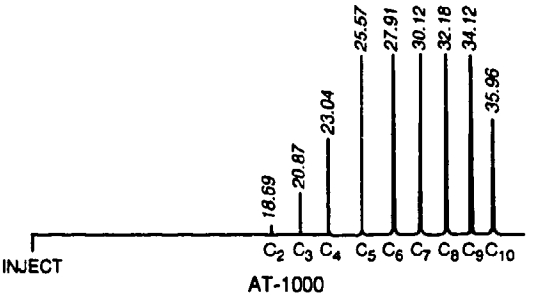


Figure 3-1. Gas chromatograms of illicit drugs and similar compounds on fused silica. A, column coated with immobilized SE-54 (FID, attenuation x 8); B column coated with immobilized OV-215 (NPD, attenuation x 128). Substances: 1 = amphetamine; 2 = phentermine; 3 = propylhexdedrine; 4 = methylamphetamine; 5 = nore phedrine; 6 = ephedrine; 7 = phenmetrazine; 8 = phendimetrazine; 9 = amfepra mone; 10 = benzocaine; 11 = phenacetine; 12 = methyphenidate; 13 = pethidine; 14 = caffeine; 15 = phenazone; 16 = lidocaine; 17 = phencylidine; 18 = procaine; 19 = dethadone; 20 = dextropropoxyphene; 21 = cocaine; 22 = codeine; 23 = diazepam; 24 = acetylmorphine; 25 = heroin; 26 = flurazepam; 27 = papaverine.

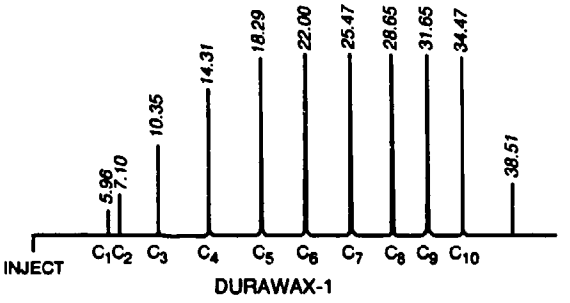
An example of dual-column correlated chromatography used to selectively identify a different class of chemicals is provided by a study of hydrocarbon oxygenate mixtures (Levy, 1984). Figure 3-2 shows dual column chromatograms for C_1-C_{10} primary alcohols, C_2-C_{10} carboxylic acids, and an example analysis of a complex mixture. This investigator reported

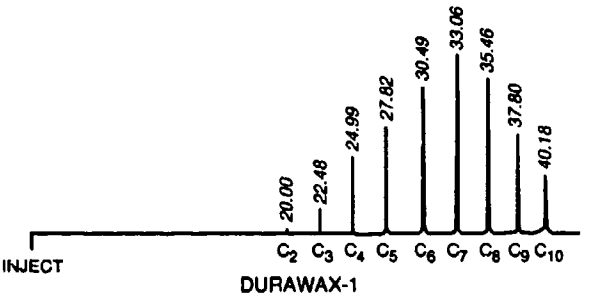


(a) Dual column chromatogram of C_1 to C_{10} primary alcohols.



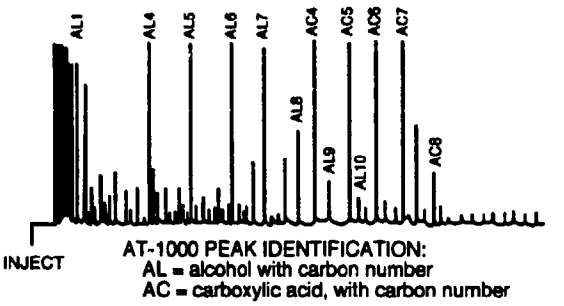
(b) Dual column chromatogram of C_2 to C_{10} carboxylic acids.

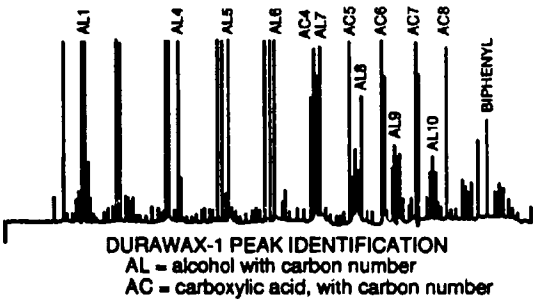




(a) Dual column chromatogram of C_1 to C_{10} primary alcohols.

(b) Dual column chromatogram of C_2 to C_{10} carboxylic acids.





(c) Dual capillary column analysis of complex oxygenate mixture.

Figure 3-2. Dual column chromatograms for primary alcohols and carboxylic acids, and an example analysis of a complex mixture.

easy determination and identification of oxygenates in hydrocarbon mixtures with excellent reproducibility.

An especially revelant example of the selectivity of correlated GC using the microchip GC technology which we have proposed for the concept instrument is provided by the research by Dr. Edward Overton's group at the Institute for Environmental Science at LSU. Their work with a correlated chromatogram database using microchip GC for EPA volatiles indicated about a 6% ambiguity for the greater than 140 volatiles in their database (Overton, 1991). These results were obtained using OV-73 and OV-1701 stationary phases, two phases which are moderately different, but do not differ nearly as much as some other possible stationary phase pairings. Dr. Overton's group has suggested to us that a 3-dimensional analysis with three different column phases would provide unparalleled selectivity for GC analysis, especially for discrimination against potentially complex chemical backgrounds.

3.2 STATIONARY PHASES FOR CORRELATED GC.

Stationary phases of interest for GC columns are chemically crosslinked and/or bonded polymers. This crosslinking or bonding provides stability and longevity to the GC column coatings to provide consistent separation performance over a long period of time compared with older approaches which consisted only of column coatings. Of particular interest are the stationary phases applied to the interior walls of capillary GC columns since these small columns provide high resolution by virtue of their small inner diameters. Typical polymers used for stationary phases used with capillary columns are substituted polysiloxanes. Common nonpolar phases are methyl substituted polysiloxanes, and more polar phases typically include increasing percentages of phenyl, cyanopropyl, or other chemical functionalities. Increasing the polarity often increases the stationary phase selectivity, although choice of a phase which interacts too strongly with materials can result in broadened and less intense peaks.

Some standard phases which are particularly of interest to this program are listed in Table 3-1. For reference, DB-5, OV-73 and SE-54 are relatively standard nonpolar phases for use in capillary GC. The DB- or OV- 210's or 225's are example choices of stationary phases which still have a significant amount of methyl substitution in their composition for good stability, but differ substantially in their polar character from the nonpolar DB-5, OV-73 and SE-54 columns. Especially interesting is the fluorinated polar character of the DB-210 and OV-210 columns. These columns simultaneously increase the polar character and column selectivity for the separation of more polar compounds and decrease the selectivity of hydrocarbons. This type of separation can be especially helpful for discriminating against common organic volatiles which are commonly found in the air as pollutants or hydrocarbon exhaust fumes.

Table 3-1. Chemical functionalities in selected stationary phases for GC.

Phase	Methyl-	Phenyl-	Cyanopropyl-	Other
SE-30	100%			
OV-101	100%			
DB-1	100%			
OV-73	94%	5%		1% vinyl
SE-54	94%	5%		1% vinyl
DB-5	94%	5%		1% vinyl
OV-17	50%	50%		
DB-17	50%	50%		
OV-210	50%			50% trifluoropropyl
DB-210	50%			50% trifluoropropyl
OV-225	50%	25%	25%	
DB-225	50%	25%	25%	
DB-1301	94%	3%	3%	
OV-1701	88%	6%	6%	
DB-1701	88%	6%	6%	
SP-2230	25%		75%	
DB-2330	25%		75%	

Based upon these considerations, DB-5 and DB-210 columns are suggested for initial consideration for the concept μGC instrument. DB-5 is a standard nonpolar stationary phase which is highly regarded for its general separation capability and stability. For contrast, DB-210 is a much different phase which is also robust and provides both a relative acceleration of hydrocarbon elution times and a retardation of the elution of polar compounds. Since many of the CW materials are polar organics (organophosphates, thiolates, amines, halogenated organics, etc.), DB-210 will effectively retard these materials relative to DB-5 while accelerating nonpolar background organics. DB-210 is not as commonly used a stationary phase as is DB-5, but it has been successfully used for chromatography with the primary CW agents in Schedule 1 (Weinberg, 1986). Further, it is commercially available for small inside diameter capillary columns for high resolution GC applications.

3.3 ADSORBENT TRAPS FOR VAPOR PRECONCENTRATION.

The sensitivity of the standard μGC detectors is about 1 ppm (parts per million). These detectors are specially fabricated by Microsensor Technology Inc. to have very small volumes and fast response for use with small inside diameter, fast GC columns. Sensitivities in the 1-10 ppm range are typical for field portable gas chromatographs used as gas analyzers. Since our projected operational requirements call for sensitivity down in the range of 10 ppb (parts per billion), preconcentration is expected to be necessary in order to detect these levels. Preconcentration has been demonstrated with μGC instrumentation to achieve sensitivities in this range (Overton, 1989).

Preconcentration can be achieved in different ways, but the most common methods for fast GC are either the use of adsorbent trapping materials or cryotrapping methods. In the adsorbent trap method of preconcentration, air containing vapors is passed through a bed of adsorbent material containing surface sites which adsorb the vapors from the air. When the adsorbent bed is heated (this process is termed "thermal desorption"), the vapors are released from the trap into a smaller volume of carrier gas which is fed through the GC. This usually involves a so-called "trap" bed of adsorbent which can be valved into the carrier gas flow of the GC concurrent with rapid heating of the trap material. The cryotrapping approach instead

involves the condensation of vapors onto chilled surfaces such as the capillary column walls cooled by liquid nitrogen, the expansion of compressed gas through a nozzle, or a thermoelectric cooler. Similarly, the condensed volatiles are rapidly heated into a smaller volume of carrier gas to achieve the preconcentration.

Volatiles and semivolatiles including or representing the CW materials in the three schedules are easily trapped using adsorbent trapping materials (Witkiewicz, 1990). A wide range of trapping materials has been investigated for this purpose which include activated carbon, silica gel, Tenax, Porapak and Chromosorb porous polymers, XAD resins, and foams. Of these materials, the most widely used are activated carbon and Tenax. Often, mixtures of adsorbent materials are also used in order to tailor the adsorption to best trap the volatiles and semivolatiles of interest. Activated carbon effectively adsorbs a very wide range of materials while relatively rejecting water vapor, but in the case of CW materials, it may induce the decomposition of organophosphorus compounds (Witkiewicz, 1990). This may not be a critical problem for activated carbon if the decomposition products provide a reproducible signature for the parent compound. In fact, several of the more reactive synthetic reagents in Schedule 2 may be too reactive to be detected directly, but instead may be detected by "ghost" peaks arising from thermal decomposition of the parent compound on the adsorbent traps (Witkiewicz, 1990). Examples are hydrogen cyanide, phosgene, and cyanogen chloride.

The adsorbent surface of Tenax is aromatic in character with ether linkages (U.S. EPA, 1978) compared to a graphite-like surface of an activated carbon such as Carbotrap (Suppelco, 1986). The relatively increased polarity of its surface due to localized surface charges can result in increased adsorption of polar organics relative to activated carbon, but at the same time it is considered to be less inducive to decomposition with some polar materials such as the organophosphorus compounds (Witkiewicz, 1990).

The ease of use and substitution of one trapping material for another suggests that we consider both Tenax and activated carbon trapping materials for the concept instrument. It is easy to substitute trapping materials which allows both trapping materials to be readily evaluated for the materials of interest. The decomposition cited for activated carbon may be

a problem with the use of activated carbon traps only if the decomposition is not reproducible in the presence of other materials on a trap resulting in inconsistent thermal desorption products. This can be evaluated in the course of instrument development and testing with different trap materials and simulants.

3.4 LABORATORY GC/MS METHODS.

For the purposes of analyzing chromatograms and simulating the performance of the concept instrument, laboratory GC/MS instrumentation can be used. This instrumentation can measure GC separations using stationary phases of choice in the normal laboratory time frame for GC measurements. As shown earlier in Figure 1-2, this time scale is in 10's of minutes rather than 10's of seconds. Different trapping materials can be tested by connecting a standard thermal desorber apparatus to the GC. The use of GC/MS is especially useful for examining the chromatograms of unknowns such as background since the mass spectrum of each peak provides some structural information about the compound responsible for the peak. High fidelity correlations are possible using the mass spectrum to characterize the components in chromatograms.

While high fidelity correlation is a good resource to have, some of the experimental encumbrances of GC/MS have made this instrumentation less than ideal for simulating the performance of correlated GC in several instances. For example, while we have speculated at this time that simultaneous isothermal chromatography at two different temperatures may provide the ideal solution to the requirements of the concept instrument, conducting isothermal measurements at high temperatures is awkward with our current laboratory GC/MS configurations using thermal desorption because of the need to cryofocus on the GC column to achieve high resolution. Cryofocusing in the GC oven is awkward for high temperature isothermal GC operation. The use of direct sample injection in lieu of cryofocusing could potentially bypass this problem, but the use of solvents for the injections has presented a background problem in many of the runs. Further, it is difficult to identically load and desorb two different traps so that a pair of chromatograms can be quantitatively correlated to a high degree of precision. In order to generate data for the analysis of quantitative approaches to

correlating simultaneous chromatograms, it is very difficult to prepare exactly matched samples for GC/MS chromatographic pairs which are independently run. For this reason, the anticipated availability of μGC instrumentation early in the program for functional elements evaluation is expected to provide a better approach toward gathering correlated test data which are quantitatively balanced by using vapor desorption from a single trap to a pair of GC modules. The availability of this instrumentation will also permit straightforward isothermal operation at a variety of temperatures.

In considering the use of GC/MS to measure and correlate chromatograms to simulate the performance of a correlated μGC, two detection modes can be considered for the concept instrument: differential detection and direct detection. This primarily applies to the correlation of environmental backgrounds for the purpose of testing detector selectivity. In differential detection, the concept instrument would first measure the air background at the inspection site and then check subsequent measurements for increases of a chemical vapor component above these levels. For GC/MS to simulate this approach, the total ion chromatograms can be background corrected by subtraction with ion chromatograms measured for vapor background. Rather than subtracting total ion intensities, though, the background correction is done according to the specific ions in the mass spectral domain. This complex correction can be done a segment of the chromatogram at a time using cross correlation methods to optimize the background correction. For simulating the direct detection mode, uncorrected GC/MS total ion chromatograms should be used for the analysis of the vapor backgrounds.

SECTION 4
DATABASE DEVELOPMENT/ANALYSIS

The third subtask of Task 1 is the development of a database for CW agents and precursors. This database of GC retention indices at various temperatures is necessary to ensure that the design range and operational parameters of the instrument are suitable for the types of separations required.

In developing this database, hydrocarbons can be used as retention time simulants for Schedule 1 materials based on extensive published retention indices values available in the open literature. Our experimental approach in this work is to run isothermal rather than conventional temperature-programmed chromatograms, since we anticipate the requirement of isothermal operation for fast, low power operation of a handheld instrument. Laboratory measurements are being carried out on selected Schedule 2 and 3 materials to survey the representive separations which need to be achieved by the handheld instrument.

Among the issues we have explored are: whether reasonable length isothermal chromatograms can be made with simulants for the heavier CW materials without exceeding the temperature limits of existing μGC components; chromatographic correlations of Schedule 2 and 3 materials to characterize potential instrument performance; bracketing of many of the Schedule 1 materials using retention index simulants; chromatographic correlation of volatiles from organic chemical storage sites; and correlation chromatography of representative organophosphorous insecticides.

The chromatographic elution of several Schedule 1 CW agents on a DB-5 capillary column relative to retention index standards was shown for a temperatured programmed GC run in Figure 2-1. The n-alkane hydrocarbons which are most commonly used as retention index standards are indicated by C together with the number of carbons (i.e., the carbon chain length). This shows for example that the C_{17} n-alkane is a good simulant for the retention time of the nerve agent VX on this particular column. The elution times of the heavy

hydrocarbons shown in Figure 2-1 are representative of the least volatile liquids in the schedules.

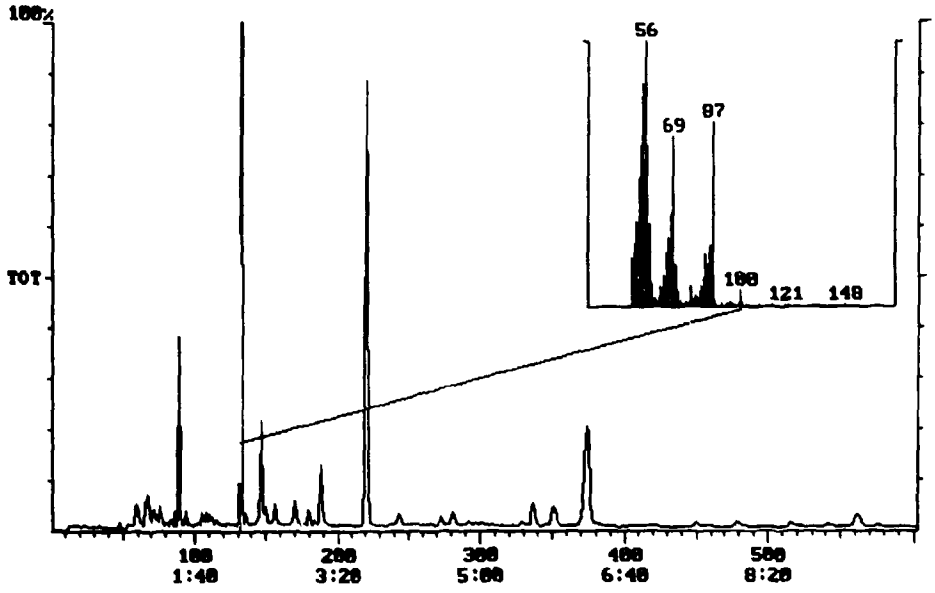
Generally CW agents and pre-cursors can be divided into two classes based on their volatility. The first class is the volatile compounds with vapor pressures at room temperatures of about 1 torr or more. These roughly correspond to hydrocarbon compounds with 10 or fewer carbon atoms and can be chromatographed at near ambient temperatures. For the several CW agents shown in Figure 2-1, soman (GD) is near the limit of the volatiles. The second class comprises semivolatile compounds which generally require elevated temperatures for efficient separations using gas chromatography.

4.1 VOLATILE COMPOUNDS.

The process used to develop correlated chromatograms for CW agents and pre-cursors using GC/MS laboratory studies is illustrated in Figure 4-1 for pinacolyl alcohol. Here, mass spectra are used for positive identification of correlated peaks on chromatograms run using both the DB-5 and DB-210 stationary phases. In this study, a pair of thermal desorption tubes was used to collect vapor samples of the pinacoyl alcohol in room air. The polarity of the DB-210 phase relative to the DB-5 phase is readily evidenced by the near doubling of the elution time with the DB-210 phase for this alcohol, a relatively polar organic.

In other studies, correlated chromatograms can be generated by injection of samples, as in the case of the Schedule 3 phosphites shown in Figure 4-2. These data importantly illustrate the selectivity achievable by pairing the DB-5 and DB-210 columns. As mentioned in Section 3, the partial fluorination of the DB-210 phase shortens the hydrocarbon elution times while delaying the elution of more polar compounds. With hydrocarbons eluting approximately twice the speed on the DB-210 column, the hydrocarbon correlations would correspond to a line with a slope of about 0.5 which would pass from the origin approximately through the points for trimethylphosphite and triethylphosphite. Thus, both of the triphosphates elute with relatively nonpolar character since they are fully alkylated.

DB-5



DB-210

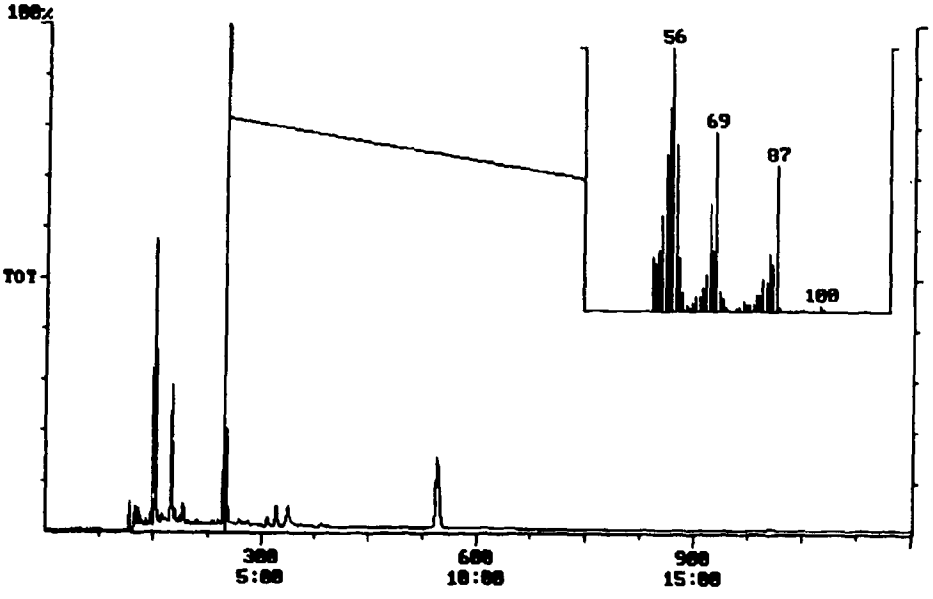


Figure 4-1. Correlation of chromatograms for pinacoyl alcohol.

However, the polar character of the diethylphosphite results in a significant increase in the elution time as shown in Figure 4-2.

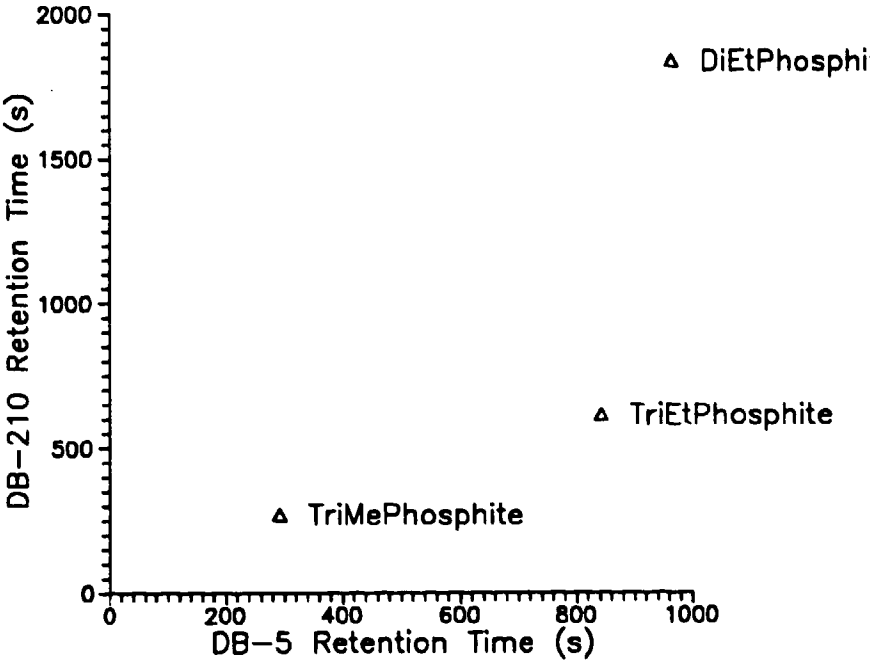


Figure 4-2. Polarity effects on relative DB-210 retention times for schedule 3 phosphites.

Correlated chromatograms for backgrounds can also be generated using GC/MS runs on air samples collected at organic chemical storage sites using adsorbant traps (such as that shown in Figures 4-3 and 4-4). The correlation of the chromatograms in Figures 4-3 and 4-4 result in the correlated chromatogram shown in Figure 4-5 for the storage site. Again, the correlated data points are strongly spread in detection space compared to similar plots with less different column pairings (Overton, 1991) with the exception of a few points which elute almost immediately following the column dead time (the time for the carrier gas to travel the length of the column). When overlayed with some relatively fast eluting and slow eluting Schedule 2 and 3 volatiles and other potential interferents such as some volatile organophorus insecticides, these results can provide a useful indication of the selectivity provided by the choice of correlated columns and chromatographic conditions, as shown in Figure 4-6. The relatively volatile organophosphate insecticides Ethion (O,O,O',O'-tetraethyl-S,S'-

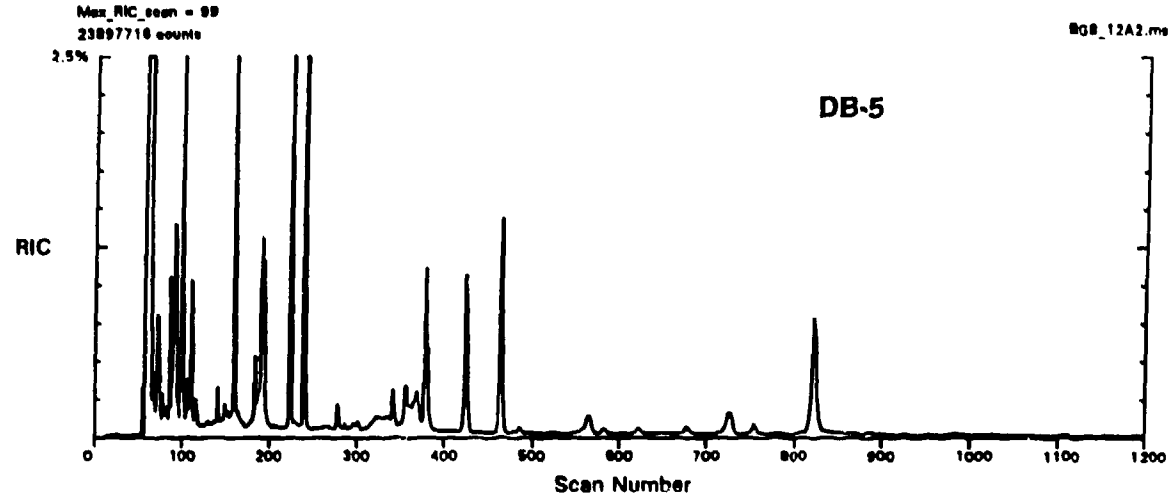


Figure 4-3. Example chromatogram for light volatiles from organic chemical storage site (isothermal, 50°C); DB-5 column.

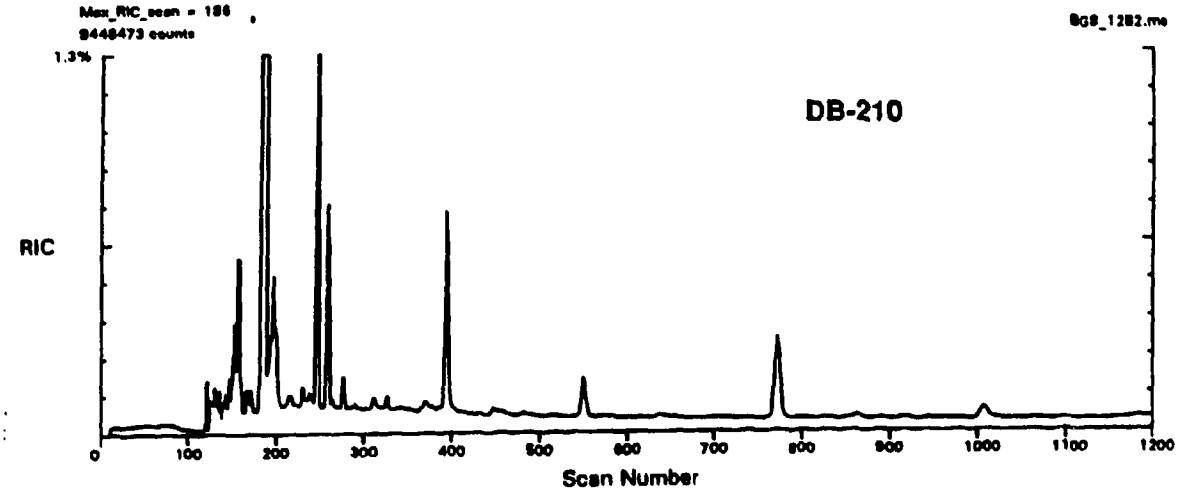


Figure 4-4. Example chromatogram for light volatiles from organic chemical storage site (isothermal, 50°C); DB-210 column.

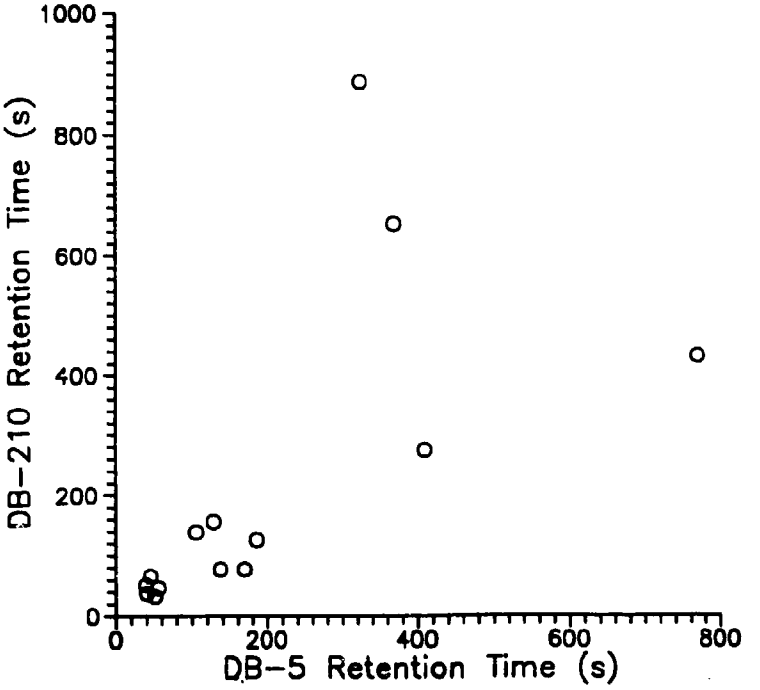


Figure 4-5. 2-D correlation of chromatograms for light volatiles from organic chemical storage site.

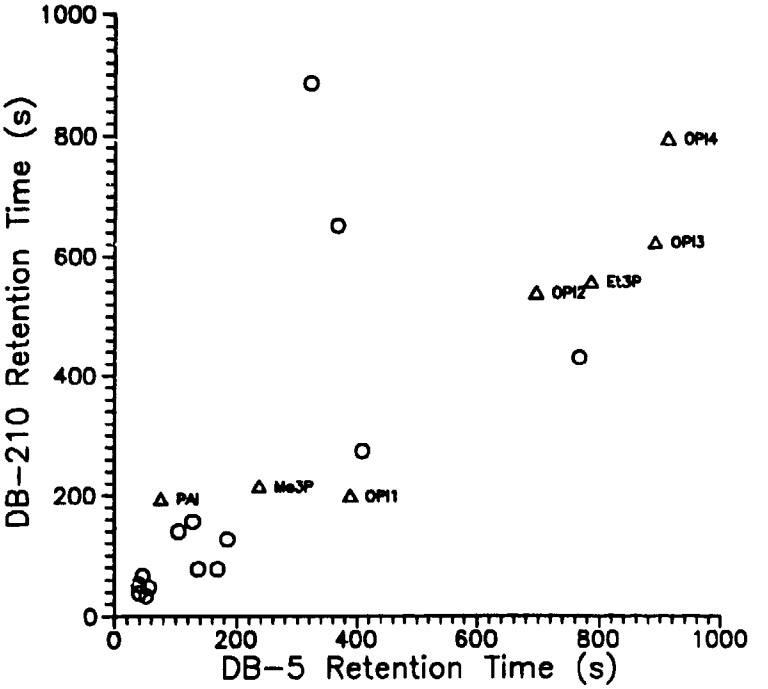


Figure 4-6. Some schedule 2 and 3 materials and organophosphorus insectides compared with background organic light volatiles.

methylenebisphosphorothioate), Di-Syston (O,O-dimethyl-S-2-[(ethylthio)-ethyl]phosphorothioate, Diazinon (O,O-diethyl-O-(2-isopropyl-4-methyl-6-pyridinyl)phosphorothioate, and Phorate (O,O-Diethyl-S-[(ehtylthio)-methyl]phosphorothioate were measured and correlated to show some representative industrial organophosphorus volatiles. While the data in Figure 4-6 are well separated in detection space, the expectation of chemically complex and highly variable background environments suggests that a very robust detection space be considered for the concept instrument. Such a detection space could consist of one additional chromatographic dimension with contrasting separation properties such as DB-225 (see Table 3-1).

4.2 SEMIVOLATILES.

As discussed above, the semivolatiles are routinely analyzed by GC, but at heated column temperatures compared to the volatiles. The retention index data shown in Figure 2-1 indicate that the least volatile CW agent materials correspond chromatographically to the heavy hydrocarbons C_{17}-C_{19}. Using the alkanes as retention time simulants for the heavier CW-related semivolatiles of interest, isothermal chromatograms were measured at a range of temperatures to determine the temperature required for a reasonable length analysis time. On the time scale of a laboratory instrument, this amounts to about 10-20 minutes, or a few hundred scans at 2 s/scan. With fast GC, the corresponding time is much faster, typically by more than an order of magnitude (see Figure 1-2).

Figure 4-7 shows the isothermal chromatograms for C_{17}-C_{20} n-alkanes at a column temperature of 170°C. The relatively shorter elution times for the hydrocarbons on DB-210 relative to DB-5 are again evident. Data before scan 120 were not collected to prevent possible damage to the electron multiplier detector by the hexane which was used as a solvent for the hydrocarbons. The correlation of these data is shown in Figure 4-8. These results suggest that the heavier semivolatiles of interest can be separated and detected quickly using fast isothermal GC by operating at elevated column temperatures in the range of 150-180°C.

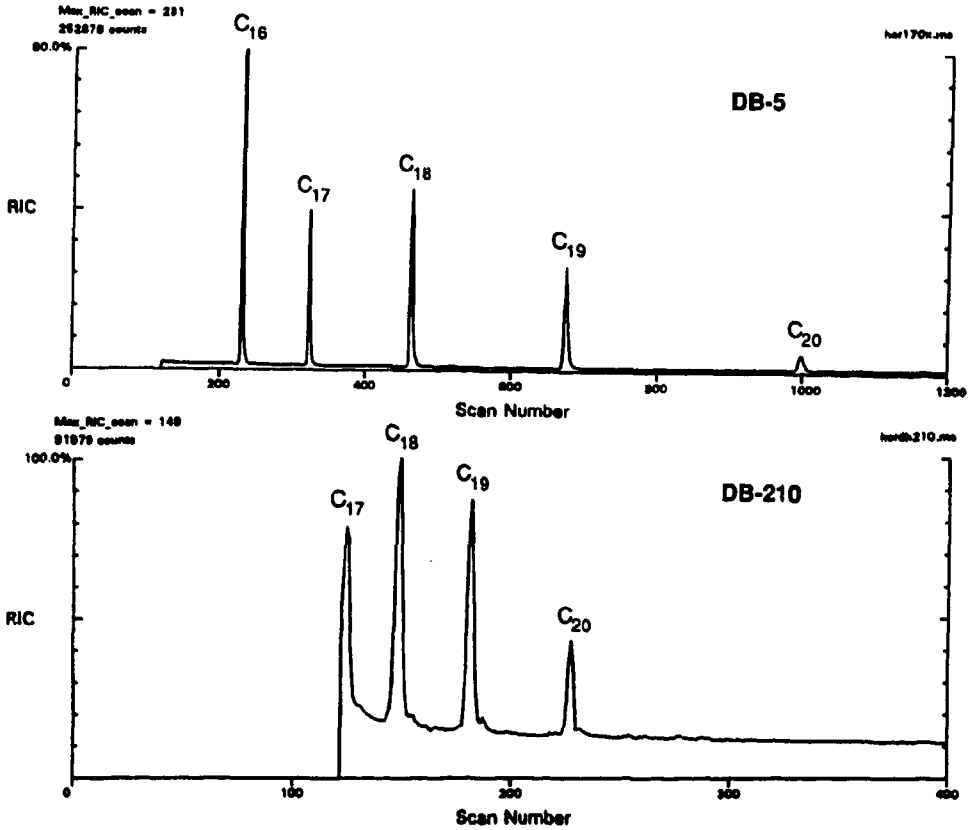


Figure 4-7. Isothermal (170°C) chromatograms of alkane simulants for heaviest CW materials.

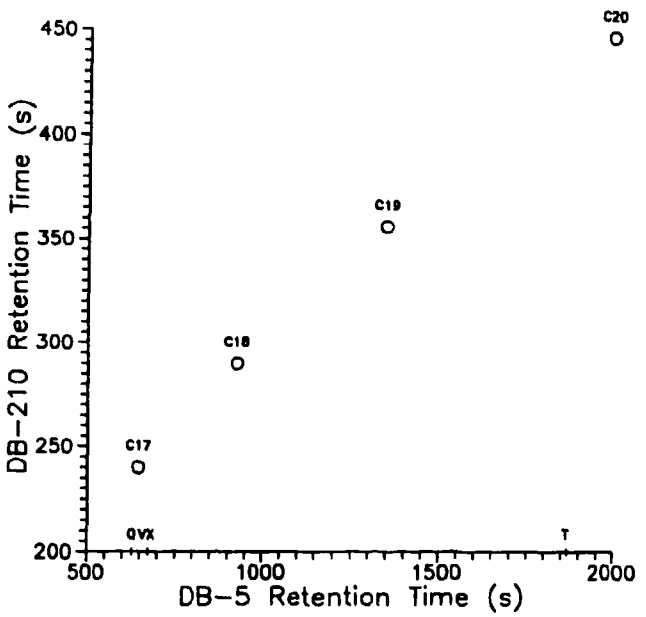


Figure 4-8. 2-D correlation plot for heavy alkane simulants.

The current generation of μGC instruments manufactured by Microsensor Technology Inc. is not fabricated with high temperature injectors. The injector components, detectors, and columns are all made to withstand temperatures in the range of 200°C and higher, but the glues used to attach the GC columns to the injector are not selected for high temperature stability. We expect that the injectors can be attached to the GC columns by other means such as soldering, and also that the injectors may not even be necessary for fast GC with the semivolatiles. Either approach can provide fast GC temperature ranges exceeding 200°C isothermal operation. Specific approaches and recommendations to extend the temperature performance of the μGC hardware for the heavier volatiles are discussed in Section 5.

SECTION 5
CONCLUSIONS & RECOMMENDATIONS

The results of these studies delineate the chromatographic performance requirements for the handheld CW detector to be capable of detecting the Schedule 1, 2 and 3 CW materials. The range of volatilities was surveyed and representative compounds and simulants were used to determine the chromatographic performance requirements. The key conclusions and recommendations based upon the results of Sections 2 through 4 of this report are as follows:

- **Two temperature regimes are likely to be needed for fast isothermal GC detection of the CW Schedules 1-3 materials.** Isothermal operation is anticipated in order to keep the analysis cycle time to a minimum (conventional temperature programming would require cooling and stabilizing after the completion of an analysis before beginning a new analysis). This would also reduce power requirements. As shown in Section 4, low molecular weight compounds chromatograph along with common volatiles as expected. With laboratory GC, elution times on the order of minutes are required for these compounds at low temperatures of only 40-50°C. Translating this to μGC instrumentation at the same temperatures, excellent separations of these materials are expected on the scale of 10's of seconds. This has recently been demonstrated for common volatiles with μGC hardware modified for this program by LSU as part of our accelerated functional elements evaluation for Task 3 of this program.

  The CW semivolatiles in Schedules 1-3 are routinely analyzed by GC, but at higher temperatures because of their lower volatility. Again, presuming the requirement for isothermal operation, GC column temperatures on the order of 150-170°C are desirable for fast separations. GC columns are normally operated at these temperatures, so the columns themselves present no difficulty. We are more concerned about the stability of the microinjector assemblies used

by Microsensor Technology Inc. for their μGC modules. Communications with MTI indicate that the injectors have been operated at temperatures in excess of 120°C, and if needed, the temperature-sensitive glue joint holding the GC column to the injector could be replaced with a deposited metal pad and soldered to a metallized column for a high temperature injector. Another possibility is that an injector is unnecessary for the semivolatiles and it could possibly be replaced altogether with an open tubular capillary column trap.

We have recommended that LSU assist GRC with the investigation of the specific design requirements for specifying the higher temperature GC module. LSU is positioned to help us quickly investigate this requirement because they have μGC test beds in place which can be used to test and specify the higher temperature performance of the μGC modular components. We currently envision a second generation handheld instrument design which contains two μGC modules, similar to the current MTI-based micromonitor that we now have, but the two μGC modules would operate at different temperatures (a low temperature module for the volatiles and a higher temperature module for the semivolatiles). As in the present micromonitor, each module would contain multiple GC columns to achieve high detection selectivity through multidimensional correlation.

- **The feasibility of developing the handheld prototype instrument utilizing μGC to detect the CW volatiles appears nearly certain.** As mentioned above, the separation of common volatiles has been experimentally demonstrated with the current dual μGC correlated column instrument which was modified for us by LSU to include microtraps. Separations are achieved in 10's of seconds under isothermal operating conditions at 40°C. The limiting sensitivity appears to be in the range of 10's of ppb. Based upon this demonstration, the feasibility of developing the handheld prototype instrument utilizing μGC to detect the CW volatiles appears to be excellent.

- **The chemical selectivity provided by 2-dimensional GC using DB-5 and DB-210 capillary columns may meet the selectivity requirements of the concept instrument, but 3-dimensional GC may be preferable for very complex chemical backgrounds and the extension of the current 2-D modules to 3-D operation is not expected to be difficult.** Our choice of the DB-5 and DB-210 stationary phase pairings has turned out to provide an excellent spread of different compounds in the 2-D correlated detection space. Not only does DB-210 separate polar compounds much differently than DB-5, but it also separates nonpolar materials very differently due to its partially fluorinated composition. Still, increased detection selectivity may be obtained through chromatographic correlation with yet a third stationary phase. This may be especially important in the event that the handheld detector is subjected to very complex chemical environments. The engineering to accomplish this may be straightforward while remaining within the physical confines of the 2-D modules. We recommend that this be considered further in the signal processing requirements analysis conducted in Task 2 of the program.

- **The choice of trap adsorbent in the concept instrument is not a major development issue.** Since it is straightforward to switch adsorbent materials in the traps, we will have the flexibility to select or change trap composition to best meet the preconcentration needs of the instrument's GC modules. According to the literature, Tenax is recommended for organophosphorus compounds, but our qualitative results indicate suitable thermal desorption of several of the CW compounds using activated carbon. Trap composition will remain a flexible component of the instrument design.

Based upon these results and recommendations, we expect in the months ahead to conduct the following activities: work with LSU to specify the design and demonstrate a high temperature μGC module for the CW semivolatiles; refine the microtrap operation of the LSU-modified MTI hardware to split a single vapor sample quantitatively between two μGC modules for generating data for the signal processing tasks; evaluate the design modifications

required for extending current μGC operation from 2-D to 3-D operation; and evaluate and specify the signal processing requirements for the concept instrument.

SECTION 6

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SUBJECT: DOCUMENT CHANGES

The Defense Threat Reduction Agency Security Office reviewed the following documents in accordance with the Deputy Secretary of Defense Memorandum entitled, "Department of Defense Initiatives on Persian Gulf War Veterans' Illnesses" dated 22 March 1995, and determined that the documents were unclassified and cleared for public release:

DNA-TR-93-84, AD-B244408, Acoustic Resonance Spectroscopy in CW Verification Tooele Field Trial (August 1992).
DNA-TR-93-129-V1, AD-B192045, Global Proliferation – Dynamics, Acquisition Strategies and Responses, Volume 1 – Overview.
DNA-TR-93-129-V2, AD-B192046, Global Proliferation – Dynamics, Acquisition Strategies and Responses, Volume 2 – Nuclear Proliferation.
DNA-TR-91-216, AD-B163637, Harmonizing the Chemical Weapons Convention with the United States Constitution.
DNA-TR-92-180, AD-B175230, Evaluation of the Concept of a List for the BWC.
DNA-TR-92-61, AD-B167663, Basic State Party Functions and Skills Under CWC.
DNA-TR-92-66, AD-B167357, Domestic Reporting Requirements for Chemical Industry.
DNA-TR-91-213, AD-B163260, Analysis of the Interactions Between Treaties.
DNA-TR-93-70, AD-B177262, Chemical Weapons Convention Inspections of Private Facilities Application of United States Environmental and Safety Laws.
DNA-TR-92-182, AD-B173450, Commercial Products from Demilitarization Operations.
DNA-TR-91-217-V3, AD-B169350, Chemical Weapons Process Parameters, Volume 3 – Users' Guide.
DNA-TR-92-116-SUP, AD-B175292, Technical Ramifications of Inclusion of Toxins in the Chemical Weapons Convention (CWC), Supplement.
DNA-TR-92-128, AD-B175452, Task 1 Report Target Vapor Identification and Database Development.
DNA-TR-92-196, AD-B174940, Task 2 Report Algorithm Development and Performance Analysis.
DNA-TR-93-68, AD-B178109, CW Detection Instrument R&D Design Evaluation.

Enclosed is a copy of the referenced memorandum. If you have any questions, please call me at 703-325-1034.

Ardith Jarrett

ARDITH JARRETT
Chief, Technical Resource Center